

# Structure of a Molybdenum Complex Containing an Uncommon Bonding Mode of PPh<sub>3</sub>.

D. Szalda (Baruch College), T. Cheng and M. Bullock (BNL)

Abstract No. Szal1002

Beamline(s): X7B

**Introduction:** The triphenylphosphine ligand is important in organometallic chemistry and homogeneous catalysis. Normally it binds to the metal through the lone pair of electrons on the phosphorus atom. In **1** it not only binds to the metal through the phosphorus but it also binds through one of the C=C bonds of one of the phenyls. In this complex the triphenylphosphine ligand acts as a chelating four-electron donor. We have recently reported (T-Y. Cheng, et al, 1999) the results of the structural characterization of **1** from data measured at X7B.

**Methods and Materials:** Crystals of **1** were grown from a mixture of toluene, methylene chloride and hexanes. Crystals of **1** were originally studied using a conventional x-ray source (sealed tube). The structures of two crystalline forms of **1** were solved using this data but there was not a sufficient number of observed data for a complete refinement for either crystal. The first crystal was triclinic without a toluene of crystallization. The second crystal was monoclinic containing a toluene of crystallization. A crystal of the monoclinic form was selected for further studies using x-rays at the National Synchrotron Light Source. Because the crystals were small and poor diffractors of x-rays, a crystal of **1** was coated with perfluoropolyether oil and mounted on the end of a glass capillary and the data collected at 95K. The data were collected by the rotation method using image plates. The data were processed and merged with Denzo/Scalepack (Z. Otwinowski and W. Minor, 1997) and the structure was refined using the SHELXTL package (G. Sheldrick, 1995).

**Results:** A drawing of the cation of **1** is presented in **Figure 1**. The cation consists of a molybdenum ion, which has two carbonyl ligands, a cyclopentadienyl ligand and a triphenylphosphine ligand coordinated to it. The coordination sphere also contains one of the phenyl rings of the triphenylphosphine, which is bent around, and  $\eta^2$  coordinated through C(31) and C(32) to the molybdenum. The Mo-P-C(31) bond angle is 73.0(3)°. The Mo-C(31) distance is 2.566(9)Å and Mo-C(32) distance is 2.649(9)Å. The Mo-H(32) distance is 2.64Å. In addition the C-C bond lengths within the phenyl which is  $\eta^2$  coordinated to the molybdenum alternate between long and short (1.36-1.45Å) whereas in the other two phenyl groups the range is smaller (1.36-1.40Å and 1.38-1.41Å).

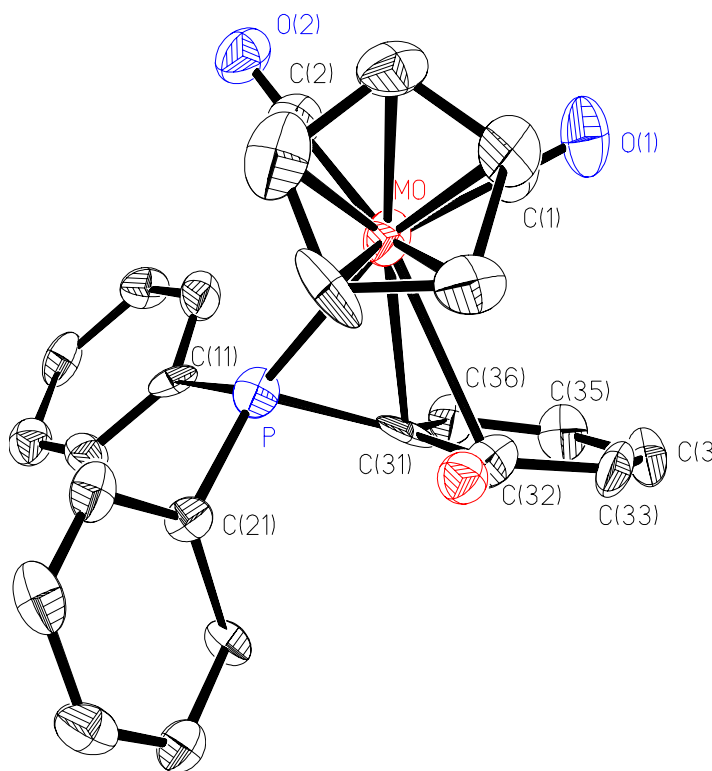
**Conclusions:** The interaction between the metal center and one of the phenyl groups of the triphenylphosphine ligand, which is observed in **1**, is unique. The most striking geometric difference between the compounds that contain a PPh<sub>3</sub> group that has an agostic interaction with a metal and the  $\eta^2$  coordination observed here can be found in the M-P-C bond angle. For agostic interactions this angle is near 114° while in **1** it is 73.0(3)°.

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G.M. Sheldrick, SHELXTL, Version 5.0. Siemens Analytical X-ray Instruments Inc. Madison, WI, USA, 1995.



**Figure 1.** The cation of [Mo(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)]{B(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, **1**. Hydrogen atoms except for H32 are omitted for clarity.